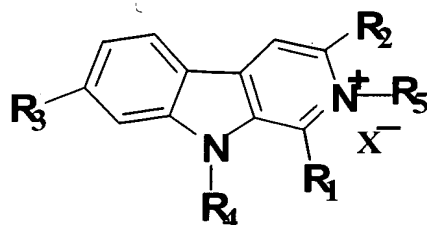


The Claims

1. A compound of the following formula (I)



wherein

R₁ is hydrogen, (secondary or tertiary) C₁₋₆ linear or secondary or tertiary branched alkyl, C₆₋₁₀ arylalkyl or 1-5 halogenated arylalkyl, heterocyclic group or alkenyl;

R₂ is hydrogen, carboxyl, ester group, carboxylate, acylamino, acyl halide group or C₁₋₆ alkoxy carbonyl, aryloxy carbonyl, or heterocyclic oxy carbonyl;

R₃ is hydrogen, hydroxyl, C₁₋₆ alkoxy, carboxylic esters, carboxylic salts, arylalkoxy, or heterocyclic oxy group;

R₄ is hydrogen, C₁₋₆ alkyl, C₁₋₆ hydroxyalkyl, C₆₋₁₀ arylalkyl or 1-5 halogenated arylalkyl, arylhydrocarbyl, arylcarboxyl, aryl ester group, arylamino group, aryl nitro group, or heterocyclic group;

R₅ is hydrogen, C₁₋₆ primary, secondary and tertiary linear or branched alkyl, C₆₋₁₀ arylalkyl and 1-5 substituted arylalkyl, or heterocyclic group or alkenyl; and

R₁, R₂, R₃ and R₄ do not represent hydrogen at the same time, and

R₁, R₂, R₃ and R₄ do not represent hydrogen at the same time,

When R₂ and R₄ are hydrogen, R₁ is not methyl and R₃ is not methoxy;

When R₁ is methyl, R₂, R₃ and R₄ do not represent hydrogen at the

same time;

When R_1 is methyl, R_2 is hydrogen, and R_3 is methoxy, R_4 is not methyl, ethyl or butyl; and

When R_1 and R_3 are hydrogen, R_2 is not methoxycarbonyl and R_4 is not methyl.

2. The compound according to claim 1, characterized in that R_1 is hydrogen or C_{1-4} alkyl or C_{6-8} arylalkyl.

3. The compound according to claim 2, characterized in that R_1 is hydrogen or C_{1-2} alkyl.

4. The compound according to claim 3, characterized in that R_1 is hydrogen.

5. The compound according to claim 1, characterized in that R_2 is hydrogen or C_{1-4} alkoxy carbonyl.

6. The compound according to claim 5, characterized in that R_2 is hydrogen or C_{1-2} alkoxy carbonyl.

7. The compound according to claim 6, characterized in that R_2 is ethoxycarbonyl.

8. The compound according to claim 1, characterized in that R_3 is hydrogen, hydroxyl or C_{1-4} alkyloxy.

9. The compound according to claim 8, characterized in that R_3 is hydrogen.

10. The compound according to claim 1, characterized in that R_4 is hydrogen, C_{1-4} alkyl, C_{1-4} hydroxyalkyl or C_{6-8} arylalkyl or substituted arylalkyl.

11. The compound according to claim 10, characterized in that R_4 is hydrogen, C_{1-2} alkyl, C_{1-2} hydroxyalkyl or C_{6-8} arylalkyl or substituted arylalkyl.

12. The compound according to claim 11, characterized in that R_4 is ethyl or benzyl.

13. The compound according to claim 12, characterized in that R₄ is benzyl.

14. The compound according to claim 1, characterized in that R₁ is hydrogen, C₁₋₄ alkyl or C₆₋₈ arylalkyl, R₂ is hydrogen, or C₁₋₄ alkoxy carbonyl, R₃ is hydrogen, hydroxyl, or C₁₋₄ alkoxy, R₄ is hydrogen or C₁₋₂ alkyl, C₁₋₂ hydroxyalkyl, C₆₋₈ arylalkyl or substituted arylalkyl.

15. The compound according to claim 14, characterized in that R₁ is hydrogen, R₂ is C₁₋₂ alkoxy carbonyl, R₃ is hydrogen, and R₄ is C₁₋₂ alkyl or C₆₋₈ arylalkyl or substituted arylalkyl.

16. The compound according to claim 15, characterized in that R₁ is hydrogen, R₂ is ethoxycarbonyl, R₃ is hydrogen, and R₄ is ethyl or benzyl.

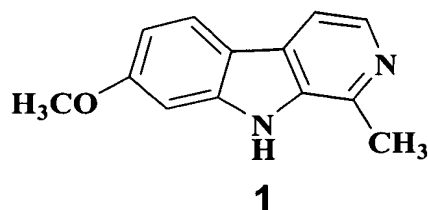
17. The compound according to claim 16, characterized in that R₁ is hydrogen, R₂ is ethoxycarbonyl, R₃ is hydrogen, and R₄ is benzyl.

18. The compound according to claim 1, characterized in that R₁ is methyl, R₂ is ethoxycarbonyl, R₃ is hydrogen, R₄ is pentafluorobenzyl, and R₅ is hydrogen.

19. The compound according to claim 1, characterized in that most preferably, R₁ is hydrogen, R₂ is hydrogen, R₃ is hydrogen, R₄ is benzyl, R₅ is benzyl, and X is bromine.

20. A process for preparing the compound according to claim 1 comprising the following steps:

1) dissolving harmines of the following formula 1 into an organic solvent or a mixed organic solvent;



2) adding 60% NaH and stirring it until there is no bubble formed;

3) adding halogenated alkane or halogenated aromatic alkane;

4) stirring and reacting said mixture at room temperature for 1-5 h;
and

5) subjecting said mixture to conventional post-treatment and purification to produce 1,7,9-trisubstituted β -carboline derivatives.

21. A process for preparing the compound according to claim 1 comprising the following steps:

1) dissolving L-tryptophan and NaOH in water;

2) adding formaldehyde;

3) stirring and refluxing said mixture by heating for 3 h; and

4) subjecting said mixture to conventional post-treatment to produce 1,2,3,4-tetrahydro- β -carboline-3-carboxylic acid (9a).

22. A process for preparing the compound according to claim 1 comprising the following steps:

1) dissolving β -carboline-3-carboxylate into an organic solvent or a mixed organic solvent;

2) adding NaH and stirring it until there is no bubble formed;

3) adding halogenated alkane or halogenated aromatic alkane;

4) stirring and reacting said mixture at room temperature, or by heating for 2 to 5 h; and

5) subjecting said mixture to conventional post-treatment and purification to produce 9-substituted- β -carboline-3-carboxylates.

23. A process for preparing the compound according to claim 1 comprising the following steps:

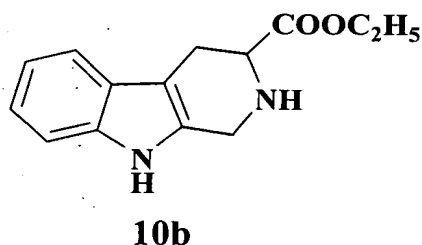
1) dissolving 1-substituted- β -carboline-3-carboxylate into an organic solvent;

2) adding 60% NaH and stirring it for 5 minutes;

- 3) adding halogenated alkane or halogenated aromatic alkane;
- 4) reacting said mixture at room temperature, or refluxing said mixture by heating; and
- 5) after the reaction is finished, subjecting said mixture to conventional post-treatment and purification to produce 9-substituted-1-methyl- β -carboline-3-carboxylates.

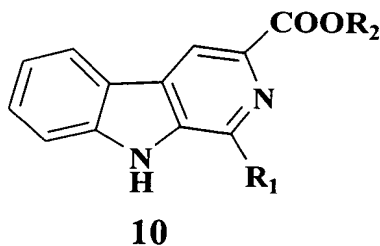
24. A process for preparing the compound according to claim 1 comprising the following steps:

- 1) mixing compound 10b of the following formula with glacial acetic acid,



- 2) adding selenium dioxide;
 - 3) refluxing said mixture by heating for 12 h; and
 - 4) subjecting the mixture to conventional post-treatment and purification to produce β -carboline.
25. A process for preparing the compound according to claim 1 comprising the following steps:

- 1) mixing compound 10 of the following formula with an organic solvent and 60% NaH;



wherein $R_1 = H$ and $R_2 = C_2H_5$;

- 2) stirring and reacting said mixture at room temperature for 5

minutes;

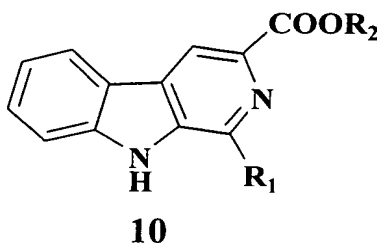
3) adding benzyl iodide;

4) stirring and reacting the mixture at a temperature of from 50 to 70°C for 2 h; and

5) subjecting the mixture to conventional post-treatment and purification to produce 2,9-dibenzyl-3-ethoxycarbonyl- β -carbolinium iodate.

26. A process for preparing the compound according to claim 1 comprising the following steps:

1) mixing compound 10 of the following formula with an organic solvent and 60% NaH;



wherein $R_1=H$ and $R_2=C_2H_5$;

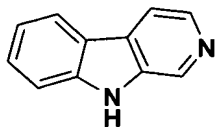
2) adding benzyl bromide;

3) stirring and reacting said mixture at a temperature of from 50 to 70°C for 5 h; and

5) subjecting the mixture to conventional post-treatment and purification to produce 2,9-dibenzyl-3-ethoxycarbonyl- β -carbolinium bromate.

27. A process for preparing the compound according to claim 1 comprising the following steps:

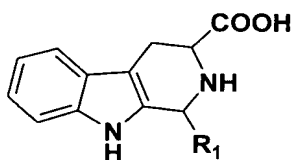
1) mixing compound 80 of the following formula with an organic solvent and 60% NaH;



80

- 2) adding benzyl bromide or benzyl iodide;
- 3) stirring and reacting said mixture at a temperature of from 50 to 70°C for 5 h; and
- 4) subjecting the mixture to conventional post-treatment and purification to produce 2,9-diphenylmethyl- β -carboline bromide or iodide salts.

28. A compound of the following formula (9a-16a):

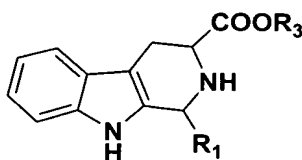


9a-16a

wherein

R₁ is methyl, ethyl, propyl, isopropyl, *n*-butyl, unsubstituted or halogenated phenyl, phenylmethyl, or phenylpropyl.

29. A compound of the following formula (9b-16b):

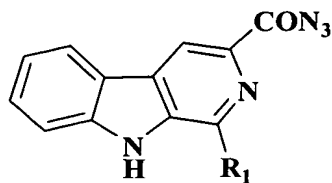


9b-16b

wherein

R₁ and R₃ are the same as R₁ defined in claim 26.

30. A compound of the following formula (21a):

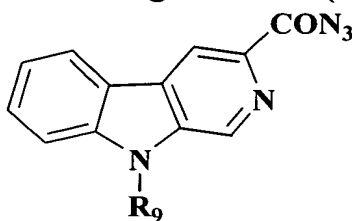


21a

wherein

R₁ is the same as R₁ defined in 26.

31. A compound of the following formula (53a-55a):

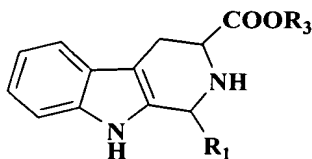


53a- 55a

wherein

R₉ is methyl, ethyl, n-butyl, phenylmethyl, phenylpropyl, polyhalogenated phenylmethyl or polyhalogenated phenylpropyl.

32. A compound of the following formula (10b):



10b

wherein

R₁ and R₃ are the same as R₁ defined in 26.

33. Use of a compound of any one of claims 1 to 18 in the manufacture of a medicament for treating tumors.

34. Use of a compound of any one of claims 1 to 18 in the manufacture of a medicament combined with phototherapy and radiation therapy for treating tumors.